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Coating material, its preparation and use to produce
firmly adhering corrosion-inhibiting coatings

The present invention relates to a novel coating
5 material curable with actinic radiation. The present
invention further relates to a novel process for
preparing a coating material curable with actinic
radiation. The present invention additionally relates
to the use of the novel coating material or of the
10 coating material prepared by means of the novel process
to produce firmly adhering corrosion-inhibiting
coatings, particularly coil coatings, especially primer
coats.

15 In order to produce firmly adhering corrosion-
inhibiting coatings on metal strips or coils,
particularly those made of the conventional utility
metals, such as zinc, aluminum or bright, galvanized,
electrolytically zinked, and phosphated steel, by means
20 of the coil coating process (Römpf Lexikon Lacke und
Druckfarben, Georg Thieme Verlag, Stuttgart, New York,
1998, page 617, "Roller coating", and page 55, "Coil
coating") it is necessary to pretreat the surface of
the metal coils. As part of the coil coating process,
25 however, this represents an additional step, which it
would be desirable to avoid on economic and technical
grounds.

As is known, primer coats serve to promote adhesion between the metal surface and the coatings lying above it. To a certain extent they may also contribute to corrosion protection. They are normally produced from pigmented, solventborne, thermally curable coating materials. However, this necessitates complex units for the suction withdrawal and disposal of the emitted solvents, and the coils must be heated to high temperatures (peak metal temperatures, PMT) in order to cure the applied coating materials at the speed which is necessary for the coil coating process. It would be highly desirable to have available solvent-free coating materials rapidly curable with actinic radiation for the production of primer coats.

Pigment-free, solvent-free coating materials (100% systems) curable with actinic radiation are known in principle. However, if these coating materials are pigmented to the high extent which would actually be necessary for sufficient corrosion protection, they become too viscous to be applied without problems, or at all, by means of roller application in the context of the coil coating process. Instead, high application temperatures and/or comparatively complicated extrusion units with slot dies must be employed, both of which are disadvantageous for the coil coating process.

In order to ensure effective protection against white rusting, i.e., the formation of zinc carbonate from zinc oxide and atmospheric carbon dioxide and water, on zinc or zinked surfaces by means of solvent-free radiation-curable coating materials alone, these materials would have to promote the rapid formation of a layer of zinc phosphate on the metal surface. However, this would only be the case at a $\text{pH} < 4$.

10 In that case, however, it would no longer be possible to use the conventional, chromate-free corrosion-inhibiting pigments based on phosphates and silicates, since these pigments are basic and give rise to high viscosity and thixotropic behavior in the coating materials.

The conventional radiation-curable aqueous dispersions, on the other hand, are always neutralized with amines, which promotes white rusting. They have a comparatively low solids content in the range of about 35 to 40% by weight, leading to a particularly high energy requirement for rapid evaporation ("flash-off") of the water. Not least, the resulting coatings remain thermoplastic and are therefore unsuitable as primer coats.

The conventional radiation-curable aqueous dispersions based on oligomers containing acrylate groups, although slightly acidic and with a somewhat higher solids

content in the region of about 50% by weight, nevertheless contain a very high amount of surface-active compounds, such as wetting agents and emulsifiers. They reduce the intercoat adhesion and the corrosion protection effect and basically can only be
5 used as additives for increasing the surface reactivity of the pigments and for improving their dispersion.

The conventional radiation-curable dispersions based on
10 polyacrylic acid contain numerous free carboxyl groups and therefore undergo immediate coagulation in acidic aqueous media.

It is an object of the present invention to provide a
15 novel, pigmented coating material which is curable with actinic radiation, substantially or entirely free from organic solvents, and which no longer has the disadvantages of the prior art but instead is easy to prepare, highly reactive and yet stable on storage,
20 particularly easy and unproblematic to apply especially as part of the coil coating process, and which can be cured very rapidly and without emitting volatile organic compounds at low curing temperatures to give coatings, particularly coil coatings, especially primer
25 coatings, which even on unpretreated metal surfaces, particularly the surface of utility metals, such as zinc, aluminum or bright, galvanized, electrolytically zinked, and phosphated steel, have particularly high adhesion, particularly high intercoat adhesion to the

overlying coatings, and an outstanding corrosion protection effect, particularly against white rust.

The invention accordingly provides the novel liquid
5 coating material in the form of a water-in-oil dispersion which is curable with actinic radiation, is substantially or completely free from organic solvents and has a $\text{pH} < 5$, comprising

10 (A) at least one constituent selected from the group consisting of low molecular mass, oligomeric, and polymeric organic compounds which contain at least one group which can be activated with actinic radiation, and also air-drying and oxidatively
15 drying alkyd resins,

(B) at least one acidic ester of polyphosphoric acid and at least one compound (b1) containing at least one hydroxyl group and at least one group which
20 can be activated with actinic radiation,

(C) at least one acidic ester of monophosphoric acid and at least one compound (c1) containing at least one hydroxyl group and at least one group which
25 can be activated with actinic radiation, and

(D) at least one acidic, corrosion-inhibiting pigment based on polyphosphoric acid.

The novel coating material is referred to below as "coating material of the invention".

The invention further provides the novel process for
5 preparing the coating material of the invention by
mixing its constituents and homogenizing the resulting
mixture, which involves

(1) mixing at least one pigment (D) in a portion of at
10 least one ester (B), at least one ester (C),
water, and a portion of the constituent or
constituents (A) and grinding the resultant
mixture in a milling apparatus to give a pigment
dispersion (1), and

15

(2) mixing a further portion of the constituent or
constituents (A) and a further portion of at least
one ester (C) with one another and homogenizing
the resulting mixture to give the makeup mixture
20 (2),

(3) then mixing the pigment dispersion (1) and the
makeup mixture (2) with one another and
homogenizing the resulting mixture to give the
25 coating material (3).

The novel process is referred to below as "process of
the invention".

In the light of the prior art it was surprising and unforeseeable for the skilled worker that the object on which the present invention was based could be achieved by means of the coating material of the invention and
5 the process of the invention.

In particular it was surprising that the inventively targeted corrosion protection effect of the coating material of the invention could be achieved by means of
10 pigments (D) which were originally envisaged for completely different purposes of application, such as the curing of waterglass (cf. Th. Staffel, F. Wahl, S. Weber and R. Glaum, "Kälte und Feuchte - na und? Polymere Aluminiumphosphate als Wasserglashärte", Farbe
15 & Lack, Volume 108, Number 10, pages 103 to 109, 2002).

Even more surprising was that the coating material of the invention no longer had the disadvantages of the prior art but instead was easy to prepare, highly
20 reactive and yet stable on storage, was particularly easy and unproblematic to apply especially as part of the coil coating process, and which could be cured very rapidly and without emitting volatile organic compounds at low curing temperatures to give coatings,
25 particularly coil coatings, especially primer coatings, which even on unpretreated metal surfaces, particularly the surface of utility metals, such as zinc, aluminum or bright, galvanized, electrolytically zinked, and phosphated steel, had particularly high adhesion,

particularly high intercoat adhesion to the overlying coatings, and an outstanding corrosion protection effect, particularly against white rust.

5 The coating material of the invention is liquid; that is, although containing solid, nonliquid constituents, it is nevertheless in a fluid state at room temperature under the conventional conditions of preparation, storage and application, and so can be processed by
10 means of the conventional application methods employed in the coil coating process.

The coating material of the invention is in the form of a water-in-oil dispersion, in which the discontinuous
15 aqueous phase is finely dispersed in the continuous organic phase. The diameter of the droplets of the aqueous phase may vary widely; preferably it is from 10 nm to 1000 μm , in particular from 100 nm to 800 μm . The constituents of the coating material of the
20 invention are distributed between the aqueous phase and the organic phase in accordance with their hydrophilicity or hydrophobicity (cf. Römpp Online, 2002, "Hydrophobicity", "Hydrophilicity"), or are present in the form of a separate solid phase.

25 The coating material of the invention or its aqueous phase has a pH < 5, preferably < 4, and in particular from 3 to 3.5.

The coating material of the invention is substantially or completely free from organic solvents. That is, its organic solvent content is $< 5\%$, preferably $< 3\%$, and more preferably $< 1\%$ by weight. In particular the amount is below the detection limits of the conventional qualitative and quantitative detection methods for organic solvents.

The coating material of the invention includes at least one constituent, preferably at least two and in particular at least three constituents, selected from the group consisting of low molecular mass, oligomeric, and polymeric organic compounds which contain at least one, especially one or at least two, group(s) which can be activated with actinic radiation, and also air-drying and oxidatively drying alkyd resins.

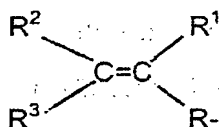
By actinic radiation is meant electromagnetic radiation, such as near infrared (NIR), visible light, UV radiation, X-rays or gamma radiation, especially UV radiation, and corpuscular radiation, such as electron beams, alpha radiation, beta radiation, proton radiation or neutron radiation, especially electron beams.

The groups which can be activated with actinic radiation contain at least one, especially one, bond which can be activated with actinic radiation. By this is meant a bond which on exposure to actinic radiation

becomes reactive and, with other activated bonds of its kind, enters into polymerization reactions and/or crosslinking reactions which proceed in accordance with free-radical and/or ionic mechanisms. Examples of suitable bonds are carbon-hydrogen single bonds or carbon-carbon, carbon-oxygen, carbon-nitrogen, carbon-phosphorus or carbon-silicon single bonds or double bonds or carbon-carbon triple bonds. Of these, the carbon-carbon double bonds and triple bonds are advantageous and are therefore used with preference in accordance with the invention. The carbon-carbon double bonds are particularly advantageous and so are used with particular preference. For the sake of brevity they are referred to below as "double bonds".

15

The double bonds are preferably contained in groups of the general formula I:



20

In the general formula I the variables have the following meanings:

R is a carbon-carbon single bond to the carbon atom of a carbonyloxy group or a divalent organic radical, preferably a carbon-carbon single bond; and

25

R^1 , R^2 and R^3 are each a hydrogen atom or an organic radical;

5 it being possible for at least two of the radicals R , R^1 , R^2 , and R^3 to be linked cyclically to one another.

Examples of suitable divalent organic radicals R include or consist of alkylene, cycloalkylene and/or
10 arylene groups. Highly suitable alkylene groups include a carbon atom or 2 to 6 carbon atoms. Highly suitable cycloalkylene groups contain 4 to 10, especially 6, carbon atoms. Highly suitable arylene groups contain 6 to 10, especially six, carbon atoms.

15

Examples of suitable organic radicals R^1 , R^2 , and R^3 include or consist of alkyl, cycloalkyl and/or aryl groups. Highly suitable alkyl groups contain one carbon atom or 2 to 6 carbon atoms. Highly suitable cycloalkyl
20 groups contain 4 to 10, especially 6, carbon atoms. Highly suitable aryl groups contain 6 to 10, especially 6, carbon atoms.

The organic radicals R , R^1 , R^2 , and R^3 may be
25 substituted or unsubstituted. However, the substituents must not interfere with the conduct of the process of the invention and/or inhibit the activation of the groups with actinic radiation. The organic radicals R , R^1 , R^2 , and R^3 are preferably unsubstituted.

Examples of especially suitable groups of the general formula I are vinyl, 1-methylvinyl, 1-ethylvinyl, propen-1-yl, styryl, cyclohexenyl, endomethylenecyclo-
5 hexyl, norbornenyl, and dicyclopentadienyl groups, especially vinyl groups.

Accordingly, the particularly preferred groups which can be activated with actinic radiation are
10 (meth)acrylate, ethacrylate, crotonate, cinnamate, cyclohexenecarboxylate, endomethylenecyclohexanecarboxylate, norbornenecarboxylate, and dicyclopentadienecarboxylate groups, but especially (meth)acrylate groups.

15

Examples of highly suitable low molecular mass compounds (A) are conventional reactive diluents (cf. Römpp Online, 2002, "Reactive diluents"). The reactive diluents are preferably selected from the group
20 consisting of isobornyl acrylate, dicyclopentenyl oxylethyl acrylate, N-(2-methacryloyloxyethyl)ethyleneurea, hydroxybutyl acrylate, hydroxyethyl acrylate, trimethylolpropane triacrylate, ethylene glycol diacrylate, and diethylene glycol diacrylate. In
25 particular, all of said reactive diluents (A) are used.

Oligomeric organic compounds (A) generally contain 2 to
15 monomeric building blocks; polymeric organic compounds (A) generally contain more than 10 monomeric

building blocks (cf. also Römpp Online, 2002, "Oligomers", "Polymers").

The oligomeric and polymeric organic compounds (A) may
5 hail from any of a very wide variety of oligomer and
polymer classes. Examples of suitable oligomer and
polymer classes are random, alternating and/or block,
linear and/or branched and/or comb polyaddition resins,
polycondensation resins, and addition (co)polymers of
10 ethylenically unsaturated monomers. For further details
of these terms refer to Römpp Lexikon Lacke und
Druckfarben, Georg Thieme Verlag, Stuttgart, New York,
1998, page 457, "Polyaddition" and "Polyaddition resins
(polyadducts)", and also pages 463 and 464,
15 "Polycondensates", "Polycondensation", and "Polycon-
densation resins".

Examples of highly suitable polyaddition resins and/or
polycondensation resins (A) are polyesters, alkyds,
20 polyurethanes, polylactones, polycarbonates, poly-
ethers, epoxy resin-amine adducts, polyureas,
polyamides, and polyimides.

Examples of highly suitable addition (co)polymers (A)
25 are (meth)acrylate (co)polymers and polyvinyl esters,
especially (meth)acrylate (co)polymers.

Particular preference is given to using oligourethanes
and polyurethanes (A). These are obtainable from

conventional diisocyanates and polyisocyanates and from compounds containing at least one, especially one, isocyanate-reactive functional group and at least one, especially one, of the above-described groups which can
5 be cured with actinic radiation.

Suitable diisocyanates and polyisocyanates include basically all of the conventional aliphatic, cycloaliphatic, aliphatic-cycloaliphatic, aromatic,
10 aliphatic-aromatic and/or cycloaliphatic-aromatic diisocyanates and polyisocyanates and polyisocyanate adducts that are used in the paints field, which are also referred to as paint polyisocyanates.

15 Examples of suitable diisocyanates are isophorone diisocyanate (i.e., 5-isocyanato-1-isocyanatomethyl-1,3,3-trimethylcyclohexane), 5-isocyanato-1-(2-isocyanatoethyl-1-yl)-1,3,3-trimethylcyclohexane, 5-isocyanato-1-(3-isocyanatoprop-1-yl)-1,3,3-trimethylcyclo-
20 hexane, 5-isocyanato-(4-isocyanatobut-1-yl)-1,3,3-trimethylcyclohexane, 1-isocyanato-2-(3-isocyanatoprop-1-yl)cyclohexane, 1-isocyanato-2-(3-isocyanatoethyl-1-yl)cyclohexane, 1-isocyanato-2-(4-isocyanatobut-1-yl)cyclohexane, 1,2-diisocyanatocyclobutane, 1,3-
25 diisocyanatocyclobutane, 1,2-diisocyanatocyclopentane, 1,3-diisocyanatocyclopentane, 1,2-diisocyanatocyclohexane, 1,3-diisocyanatocyclohexane, 1,4-diisocyanatocyclohexane, dicyclohexylmethane 2,4'-diisocyanate, dicyclohexylmethane 4,4'-diisocyanate,

liquid dicyclohexylmethane 4,4'-diisocyanate with a trans/trans content of up to 30% by weight, preferably 25% by weight, and in particular 20% by weight, which is obtainable by phosgenating isomer mixtures of bis(4-aminocyclohexyl)methane or by fractionally crystallizing commercially customary bis(4-isocyanatocyclohexyl)methane in accordance with patents DE 44 14 032 A1, GB 1220717 A, DE 16 18 795 A1 or DE 17 93 785 A1; trimethylene diisocyanate, tetramethylene diisocyanate, pentamethylene diisocyanate, hexamethylene diisocyanate, ethylethylene diisocyanate, trimethylhexane diisocyanate, heptamethylene diisocyanate or diisocyanates derived from dimer fatty acids as sold under the commercial designation DDI 1410 by Henkel and described in patents WO 97/49745 A and WO 97/49747 A, especially 2-heptyl-3,4-bis(9-isocyanatononyl)-1-pentylcyclohexane, 1,2-, 1,4- or 1,3-bis(isocyanatomethyl)cyclohexane, 1,2-, 1,4- or 1,3-bis(2-isocyanatoeth-1-yl)cyclohexane, 1,3-bis(3-isocyanatoprop-1-yl)cyclohexane or 1,2-, 1,4- or 1,3-bis(4-isocyanatobut-1-yl)cyclohexane, m-tetramethylxylylene diisocyanate (i.e., 1,3-bis(2-isocyanatoprop-2-yl)-benzene, toluylene diisocyanate or diphenylmethane diisocyanate.

25

Examples of suitable polyisocyanates based on the above-described diisocyanates are isocyanato-containing polyurethane prepolymers prepared by reacting polyols with an excess of at least one of the above-described

diisocyanates, and/or polyisocyanates containing isocyanurate, biuret, allophanate, iminooxadiazine-dione, urethane, urea and/or uretdione groups. It is preferred to use polyisocyanates having on average from 2 to 5 isocyanate groups per molecule and viscosities of 100 to 10 000, preferably 100 to 5000, mPas. Moreover, the polyisocyanates may have been subjected to conventional hydrophilic or hydrophobic modification.

10

Examples of suitable preparation processes are known, for example, from patents CA 2,163,591 A, US-A-4,419,513, US 4,454,317 A, EP 0 646 608 A, US 4,801,675 A, EP 0 183 976 A1, DE 40 15 155 A1, EP 0 303 150 A1, EP 0 496 208 A1, EP 0 524 500 A1, EP 0 566 037 A1, US 5,258,482 A1, US 5,290,902 A1, EP 0 649 806 A1, DE 42 29 183 A1 or EP 0 531 820 A1.

Also suitable are the high-viscosity polyisocyanates described in German patent application DE 198 28 935 A1.

Examples of suitable isocyanate-reactive functional groups are hydroxyl groups, thiol groups, and primary and secondary amino groups, especially hydroxyl groups.

Examples of especially suitable compounds containing an isocyanate-reactive functional group and a group which can be activated with actinic radiation are monomers

which carry at least one hydroxyl or amino group per molecule, such as

- hydroxyalkyl esters of acrylic acid, methacrylic acid or another alpha,beta-olefinically unsaturated carboxylic acid which derive from an alkylene glycol which is esterified with the acid or which are obtainable by reacting the alpha,beta-olefinically unsaturated carboxylic acid with an alkylene oxide such as ethylene oxide or propylene oxide, especially hydroxyalkyl esters of acrylic acid, methacrylic acid, ethacrylic acid, crotonic acid, maleic acid, fumaric acid or itaconic acid, in which the hydroxyalkyl group contains up to 20 carbon atoms, such as 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 3-hydroxybutyl, 4-hydroxybutyl acrylate, methacrylate, ethacrylate, crotonate, maleate, fumarate or itaconate; or hydroxycycloalkyl esters such as 1,4-bis(hydroxymethyl)cyclohexane, octahydro-4,7-methano-1H-indenedimethanol or methylpropanediol monoacrylate, monomethacrylate, monoethacrylate, monocrotonate, monomaleate, monofumarate or monoitaconate; reaction products of cyclic esters, such as epsilon-caprolactone, for example, and these hydroxyalkyl or hydroxycycloalkyl esters;

- olefinically unsaturated alcohols such as allyl alcohol;
- polyols such as trimethylolpropane monoallyl or diallyl ether or pentaerythritol monoallyl, diallyl or triallyl ether;
- reaction products of acrylic acid and/or methacrylic acid with the glycidyl ester of an alpha-branched monocarboxylic acid having 5 to 18 carbon atoms per molecule, especially of a Versatic® acid, or instead of the reaction product an equivalent amount of acrylic and/or methacrylic acid which is then reacted, during or after the polymerization reaction, with the glycidyl ester of an alpha-branched monocarboxylic acid having 5 to 18 carbon atoms per molecule, in particular a Versatic® acid;
- aminoethyl acrylate, aminoethyl methacrylate, allylamine or N-methyliminoethyl acrylate; and/or
- acryloyloxysilane-containing vinyl monomers, preparable by reacting hydroxy-functional silanes with epichlorohydrin and then reacting the reaction product with (meth)acrylic acid and/or hydroxyalkyl and/or hydroxycycloalkyl esters of (meth)acrylic acid and/or further hydroxyl-containing monomers.

In particular, 4-hydroxybutyl acrylate is used.

The reaction of the diisocyanates and polyisocyanates
5 with the compounds having at least one isocyanate-
reactive functional group and at least one group which
can be activated with actinic radiation has no special
features in terms of method but is instead carried out,
for example, as described in international patent
10 application WO 96/23836 A.

Air-drying and oxidatively drying alkyd resins (A),
such as linseed oil, soybean oil, safflower oil or
ricinene alkyd resins, are compounds known per se and
15 are described for example in Römpp Online, 2002, "Alkyd
resins". Preferred alkyd resins are those with an oil
length or oil content of 20 to 60%, in particular 25 to
60%. 45 to 65 eq.%, in particular 48 to 60 eq.%, of the
olefinically unsaturated double bonds present in the
20 unsaturated fatty acid residues of the alkyd resin (A)
are conjugated. On account of its oil length or oil
content, the alkyd resin is also referred to as a
medium-oil alkyd resin.

25 The unsaturated fatty acid residues of the alkyd resins
(A) are derived from unsaturated fatty acids, such as
lauroleic acid (dodecenoic acid), myristoleic acid
(tetradecenoic acid), palmitoleic acid (hexadecenoic
acid), oleic acid (octadecenoic acid), gadoleic acid

(eicosenoic acid), erucic acid (docosenoic acid), ricinoleic acid (12-hydroxyoctadecenoic acid), linoleic acid (octadecenoic acid), linolenic acid (octadecatrienoic acid), elaeostearic acid, eicosapentenoic acid or docosahexaenoic acid, which are found in and/or can be obtained from vegetable and animal oils, such as castor oil, dehydrated castor oil, coconut oil, palm oil, groundnut oil, cottonseed oil, soybean oil, safflower oil, sunflower oil, OH sunflower oil, linseed oil, high erucic acid and low erucic acid colza oil, wood oil, oiticica oil, lard, talc, sperm oil, and herring oil.

The unsaturated fatty acids are commercial products and are sold, for example, by UNIQEMA under the brand names Prifac® or Dedico®, by Henkel under the brand name Isomerginsäure® or by Akzo under the brand name Nouracid®.

The amount of fatty acid residues (oil length) and of fatty acid residues containing conjugated double bonds can easily be adjusted by the skilled worker by way of the amount of fatty acids in total and by way of the ratio of olefinically unsaturated fatty acids without conjugated double bonds to olefinically unsaturated fatty acids with conjugated double bonds.

As is known, the alkyd resins (A) are prepared from polyols and polybasic carboxylic acids and the abovementioned oxidatively drying fatty acids.

Examples of suitable polyhydric alcohols are glycerol, pentaerythritol, trimethylolethane, and trimethylolpropane.

5

Examples of suitable polybasic carboxylic acids are tetrahydrophthalic and hexahydrophthalic acid, methylnadic acid, methylenedimethylene- and 3,6-endomethylenetetrahydrophthalic acid, and also the
10 corresponding anhydrides of these acids.

The alkyd resins (A) may also be in modified form, having been modified with at least one modifying component, such as oils, natural resins, phenolic
15 resins, acrylic resins, styrene, epoxy resins, silicone resins or isocyanates.

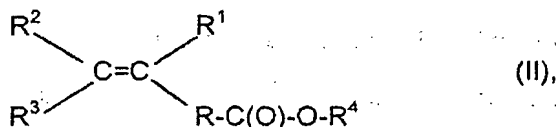
The alkyd resins (A) are commercial products and are sold, for example, under the brand name Alkydal® R 35
20 by Bayer AG, Italkyd® R35 by Multi Resin. The alkyd resins (A) are preferably solvent-free in the sense described above or are freed from organic solvents by means, for example, of distillation.

25 Particularly advantageous coating materials of the invention comprise the above-described reactive diluents (A), the oligomers and polymers (A), and the alkyd resins (A).

The coating material of the invention includes at least one, especially one, acetic ester of polyphosphoric acid and at least one compound (b1) containing at least one, especially one, hydroxyl group and at least one group which can be activated with actinic radiation. Examples of suitable groups which can be activated with actinic radiation are those described above. The diphosphorous pentoxide content of the polyphosphoric acid may vary widely; preferably it is from 60 to 95% by weight, more preferably from 70 to 95% by weight, and in particular from 70 to 90% by weight.

The coating material of the invention further includes at least one, especially one, acetic ester of monophosphoric acid and at least one compound (c1) containing at least one hydroxyl group and at least one group which can be activated with actinic radiation. Examples of suitable groups which can be activated with actinic radiation are those described above.

Highly suitable compounds (b1) and (c1) are selected from the group consisting of carboxylic esters of the general formula II:



in which the variables R, R¹, R², and R³ are as defined above and the variable R⁴ stands for a hydroxyl-containing monovalent organic radical.

- 5 The monovalent organic radical R⁴ preferably contains at least one radical which is selected from the group consisting of hydroxyl-containing alkyl, cycloalkyl, and aryl radicals, or consists thereof. It is preferred to use alkyl radicals R⁴. With particular preference,
- 10 the hydroxyl-containing alkyl radical R⁴ is a hydroxyethyl radical, a 2- or 3-hydroxypropyl radical, a 4-hydroxybutyl radical or an omega-hydroxyoligocaprolactyl radical.
- 15 Examples of especially suitable compounds (b1) are 4-hydroxybutyl acrylate and oligocaprolactone monoacrylate, preferably with a number-average molecular weight of from 250 to 500. Examples of especially suitable esters (B) of polyphosphoric acid
- 20 are 4-acryloylbut-1-yl polyphosphate and omega-acryloyloligocaprolacton-1-yl polyphosphate.

Examples of especially suitable compounds (c1) are hydroxypropyl methacrylate and hydroxyethyl

25 methacrylate. Especially suitable esters (C) of monophosphoric acid are 2-methacryloyleth-1-yl phosphate and 3-methacryloylprop-1-yl phosphate. The esters (C) are commercial products which are sold under

the brand name Sipomer® by Rhodia as wetting agents or emulsifiers.

The coating material of the invention includes not
5 least at least one, especially one, acidic, corrosion-
inhibiting pigment based on polyphosphoric acid.
Preference is given to using aluminum and zinc
polyphosphates. Aluminum polyphosphates are
conventional products and are sold, for example, under
10 the brand name Targon® HS by BK Giulini. Zinc
polyphosphates are obtainable from polyphosphoric acid
and zinc oxide. They are preferably used in the form of
an aqueous suspension.

15 Furthermore, the coating material of the invention may
comprise at least one additive (E), in particular at
least two additives (E), in effective amounts.

Additive (E) is preferably selected from the group
20 consisting of polyphosphoric acid, dryers, organic and
inorganic, colored and achromatic, optical effect,
electrically conductive, magnetically shielding, and
fluorescent pigments other than the pigments (D),
transparent and opaque, organic and inorganic fillers,
25 nanoparticles, antisetting agents, oligomeric and
polymeric binders other than the constituents (A), UV
absorbers, light stabilizers, free-radical scavengers,
photoinitiators, devolatiliziers, slip additives,
polymerization inhibitors, defoamers, emulsifiers and

wetting agents other than the constituents (C), adhesion promoters, leveling agents, film formation auxiliaries, rheology control additives, and flame retardants.

5

Particularly advantageous coating materials include polyphosphoric acid, dryers, photoinitiators, nanoparticles, such as aerosils, as antisetling agents, and emulsifiers and wetting agents other than
10 the constituents (C).

The amount of the above-described constituents in the coating material of the invention may vary widely and is guided by the requirements of the case in hand.

15

Based on the solids, i.e., the sum of the constituents which make up the coatings produced from the coating material, the coating material of the invention preferably contains 1 to 10%, more preferably 1.5 to
20 8%, in particular 2 to 6% by weight of organically bonded diphosphorous pentoxide. Based on the solids the coating material of the invention preferably contains 5 to 30%, more preferably 8 to 25%, and in particular 10 to 20% by weight of inorganically bonded diphosphorous
25 pentoxide.

The solids content of the coating material of the invention, based in each case on its total amount, is preferably 70 to 99%, more preferably 75 to 95%, and in

particular 70 to 95% by weight. The water content of the coating material of the invention, based in each case on its total amount, is preferably 1 to 30%, more preferably 5 to 25%, and in particular 5 to 30% by weight.

The proportion of pigment (D) to constituent (A) is preferably 1:0.5 to 1:10, more preferably 1:1 to 1:8, and in particular 1:1.5 to 1:6.

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Particularly advantageous coating materials of the invention contain, based in each case on their solids,

- preferably 5 to 35%, more preferably 6 to 30%, and in particular 7 to 25% by weight of an alkyd resin (A),

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- preferably 5 to 35%, more preferably 6 to 30%, and in particular 7 to 25% by weight of an oligourethane (A),

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- preferably 15 to 40%, more preferably 20 to 35%, in particular 20 to 30% by weight of a mixture of reactive diluents (A), preferably composed of isobornyl acrylate, dicyclopentenylloxyethyl acrylate, N-(2-methacryloyloxyethyl)ethyleneurea, hydroxybutyl acrylate, hydroxyethyl acrylate, trimethylolpropane triacrylate, ethylene glycol diacrylate, and diethylene glycol diacrylate,

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- preferably 1 to 10%, more preferably 2 to 8%, and in particular 3 to 7% by weight of an ester (B),
- 5 - preferably 0.1 to 3%, more preferably 0.2 to 2%, in particular 0.3 to 1.5% by weight of an ester (C),
- preferably 5 to 40%, more preferably 6 to 35%, and in particular 7 to 30% by weight of a pigment (D),
- 10 - preferably 0.1 to 3%, more preferably 0.2 to 2%, in particular 0.3 to 1.5% by weight of a non-(C) wetting agent (E),
- 15 - preferably 0.01 to 1%, more preferably 0.02 to 0.8%, and in particular 0.03 to 0.7% by weight of nanoparticles (E),
- 20 - preferably 1 to 10%, more preferably 1.5 to 9%, in particular 2 to 8% by weight of polyphosphoric acid (E),
- preferably 1 to 10%, more preferably 1.5 to 9%, and in particular 2 to 8% by weight of a photoinitiator (E), and
- 25

- preferably 0.1 to 3%, more preferably 0.2 to 2.5%, and in particular 0.3 to 2% by weight of a dryer (E).

5 Components (I) and (II) are prepared preferably by mixing the above-described constituents in suitable mixing equipment such as stirred tanks, stirred mills, extruders, kneading apparatus, Ultraturrax, inline
10 dissolvers, static mixers, micromixers, toothed wheel dispersers, pressure release nozzles and/or microfluidizers. It is preferred here to operate in the absence of light with a wavelength $\lambda < 550$ nm or in complete absence of light, in order to prevent premature crosslinking of component (I) and, where
15 appropriate, of component (II) which can be activated with actinic radiation.

The coating material of the invention is prepared preferably by mixing the above-described constituents
20 in suitable mixing equipment such as stirred tanks, stirred mills, extruders, kneading apparatus, Ultraturrax, inline dissolvers, static mixers, micromixers, toothed wheel dispersers, pressure release nozzles and/or microfluidizers. It is preferred here to
25 operate in the absence of light with a wavelength $\lambda < 550$ nm or in complete absence of light, in order to prevent premature crosslinking.

For the coating material of the invention it is of advantage if it is prepared by the process of the invention. The process of the invention involves

- 5 (1) mixing at least one pigment (D) with a portion of at least one ester (B), at least one ester (C), water, and a portion of the constituent or constituents (A) and grinding the resultant mixture in a milling apparatus to give a pigment
10 dispersion (1), and
- (2) mixing a further portion of the constituent or constituents (A) and a further portion of at least one ester (C) with one another and homogenizing
15 the resulting mixture to give the makeup mixture (2),
- (3) then mixing the pigment dispersion (1) and the makeup mixture (2) with one another and
20 homogenizing the resulting mixture to give the coating material (3).

For mixing and homogenizing it is possible to use the mixing equipment described above. The pigment
25 dispersion (1) is preferably ground to a Hegman fineness of 1 to 10, preferably 1.5 to 8, and in particular 2 to 4 μm . This can be done using the conventional grinding equipment, such as bead mills and stirred mills.

The pigment dispersion (1) and the makeup mixture (2) are preferably mixed with one another in a proportion of 3:1 to 0.33:1, more preferably 2.5:1 to 1:1, and in particular 2:1 to 1.2:1.

For preparing the pigment dispersion (1) it is preferred as constituents (A) to use at least one of the above-described alkyd resins and at least one, in particular at least two, of the above-described low molecular mass organic compounds.

For preparing the makeup mixture (2) it is preferred as constituents (A) to use at least one of the above-described alkyd resins, at least one, in particular at least two, of the above-described low molecular mass organic compounds, and at least one, especially one, of the above-described oligomeric or polymeric organic compounds.

Furthermore, for preparing the pigment dispersion (1) and the makeup mixture (2) it is possible to use at least one of the above-described additives (E). As additives (E) for preparing the pigment dispersion (1) it is preferred to use at least one, especially one, emulsifier which is different from the ester (C), or at least one, especially one, non-(C) wetting agent, and also at least one, especially one, kind of nanoparticles. As additives (E) for preparing the

makeup mixture (2) it is preferred to use polyphosphoric acid, at least one, especially one, photoinitiator, and at least one, especially one, dryer.

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In the process of the invention the constituents (A) to (E) are used preferably in amounts such as to give the above-described preferred proportions of the constituents of the coating material of the invention.

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The coating materials of the invention are outstandingly suitable for the production of coatings of all kinds. In particular they are suitable as coil coating materials. Moreover, they are outstandingly
15 suitable for producing coatings on all utility metals, in particular on bright steel, galvanized, electrolytically zinked, and phosphated steel, zinc, and aluminum, on coatings, especially primer coatings, and on SMC (sheet molded compounds) and BMC (bulk
20 molded compounds). The coatings of the invention are outstandingly suitable as clearcoats, topcoats, temporary or permanent protective coats, primer coats, sealing coats, and antifingerprint coats, but especially as primer coats.

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Surprisingly, the coatings of the invention, especially the primer coatings of the invention, even on unpretreated metal surfaces, such as on unpretreated HDG (hot dipped galvanized) steel, meet at least the

requirements of class IV of the specification of the company Usinor for components for outdoor use, particularly in terms of adhesion, flexibility, hardness, chemical resistance, intercoat adhesion, and
5 corrosion protection effect, to the full extent.

In terms of method, the application of the coating materials of the invention has no special features but can instead take place by any conventional application
10 method, such as spraying, knife coating, brushing, flow coating, dipping, trickling or rolling, for example. Generally speaking it is advisable to operate in the absence of actinic radiation, in order to prevent premature crosslinking of the coating materials
15 of the invention. Following application, the water contained in the coating material of the invention can be evaporated in a simple manner, this also being referred to as flash-off. This is preferably done by the brief inductive heating of the metal substrates.

20
Radiation sources suitable for curing the applied coating materials of the invention with actinic radiation include sources such as high or low pressure mercury vapor lamps or electron beam sources. Further
25 examples of suitable methods and apparatus for curing with actinic radiation are described in German patent application DE 198 18 735 A1, column 10 line 31 to column 11 line 22, by R. Stephen Davidson in "Exploring the Science, Technology and Applications of U.V. and

E.B. Curing", Sita Technology Ltd., London, 1999, Chapter I, "An Overview", page 16, Figure 10, or by Dipl.-Ing. Peter Klamann in "eltosch System-Kompetenz, UV-Technik, Leitfaden für Anwender", page 2, October 5 1998.

For irradiation it is preferred to use a radiation dose from 100 to 6000 mJ cm⁻², preferably 200 to 3000, more preferably 300 to 2500, and with particular preference 10 500 to 2000 mJ cm⁻².

The radiation intensity may vary widely. It is guided in particular by the radiation dose on the one hand and the irradiation time on the other. For a given 15 radiation dose, the irradiation time is guided by the belt speed or speed of advance of the substrates in the irradiation unit and vice versa. The radiation intensity is preferably 1x10⁰ to 3x10⁵, more preferably 2x10⁰ to 2x10⁵, with particular preference 3x10⁰ to 20 2.5x10⁵, and in particular 5x10⁰ to 2x10⁵ W m⁻².

It is a particular advantage of the coating material of the invention that the radiation cure can be assisted by oxidative curing in air. It is a further particular 25 advantage of the coating material of the invention that it can also be cured only partly and in this state can be overcoated with at least one further coating material, in particular with a coating material curable with actinic radiation, after which all applied films

can be cured together using actinic radiation. By this means the process times are shortened further, and the intercoat adhesion is further improved. Overall, owing to the use of the coating material of the invention, it is no longer necessary in the coil coating process to heat the metal sheets to PMTs of 240°C or more. Also unnecessary is the suction withdrawal and disposal of volatile organic compounds, so allowing the expenditure in terms of apparatus, safety technology, and energy to be reduced significantly.

The resulting coatings of the invention are highly flexible, very highly deformable without damage, resistant to chemicals, stable to weathering, resistant to condensation and salt water, and of high adhesion to the substrates and to other coatings. They combine all of these features with an outstanding visual appearance.

Examples

Example 1

The preparation of the coating material 1

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For the preparation of the coating material 1, a mixture is first prepared from 18.9 parts by weight of an alkyd resin with an oil length of 28%, a mass-average molecular weight of 10 000 to 12 000 daltons,

and a molecular weight polydispersity < 5 , based on hexahydrophthalic acid and modified sunflower oil FA having a conjugated double bond fraction of from 48 to 62 eq.%, based on the number of double bonds present (Edenor® 6010 from Henkel), 12.6 parts by weight of isobornyl acrylate, 2 parts by weight of dicyclopentenylloxyethyl acrylate, 9 parts by weight of a polyphosphoric ester of 4-hydroxybutyl acrylate (prepared by reacting 80 parts by weight of 4-hydroxybutyl acrylate and 20 parts by weight of polyphosphoric acid with a diphosphorous pentoxide content of 84% by weight; excess of 4-hydroxybutyl acrylate: 20% by weight), 17.5 parts by weight of deionized water, 7 parts by weight of Laromer® PE 55 WN (monomer mixture of trimethylolpropane triacrylate, ethylene glycol diacrylate, 2-hydroxyethyl acrylate and diethylene glycol diacrylate, 50 percent strength in water, from BASF Aktiengesellschaft), 1.5 parts by weight of Rheolate® 2001 (commercial wetting agent from Elementis), 2 parts by weight of 3-methacryloylpropyl phosphate (Sipomer® DV 6661, commercial wetting agent from Rhodia) and Aerosil® 200 (commercial anti-settling agent from Degussa). The mixture was homogenized in an Ultraturrax at a rotary speed of 1800 for 20 minutes.

30 parts by weight of an aluminum polyphosphate (Targon® HS from BK Giulini) were added to the mixture.

The resulting pigment dispersion was ground in a bead mill to a Hegman fineness of from 2 to 4 μm .

In parallel, a makeup mixture was prepared from 7.2
5 parts by weight of the above-described alkyd resin, 4.8
parts by weight of isobornyl acrylate, 35 parts by
weight of the above-described polyphosphoric ester of
4-hydroxybutyl acrylate, 5.5 parts by weight of
polyphosphoric acid (diphosphorous pentoxide content:
10 84% by weight), 28 parts by weight of an oligourethane
prepared from a modified polyisocyanate prepolymer
based on diphenylmethane diisocyanate (Desmodur® 2010
from Bayer AG) and 4-hydroxybutyl acrylate, 12 parts by
weight of dicyclopentenylloxyethyl acrylate, 5.5 parts
15 by weight of Irgacure® 184 (commercial photoinitiator
from Ciba Specialty Chemicals), 1.25 parts by weight of
cobalt octoate, and 2.5 parts by weight of N-(2-
methacryloyleth-1-yl)ethyleneurea.

20 62.5 parts by weight of the pigment dispersion were
mixed with 37.5 parts by weight of the makeup mixture,
after which the resulting coating material 1 was
homogenized.

25 The coating material 1 had a solids content of 85% by
weight, a pigment/binder ratio of 1:3, a pH of 3,
organically bonded diphosphorous pentoxide in an amount
of 4% by weight, based on the solids, and inorganically
bonded disphosphorous pentoxide in an amount of 17% by

weight, based on the solids. The coating material 1 was fully stable on storage in the absence of actinic radiation for at least one month. It was outstandingly suitable for the production of primer coatings.

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Example 2

The preparation of the coating material 2

10 Example 1 was repeated but using

- 9 parts by weight instead of 17.5 parts by weight of deionized water and

15 - 40 parts by weight of zinc polyphosphate (75% by weight in water) instead of 30 parts by weight of aluminum polyphosphate.

The coating material 2 likewise had a solids content of
20 85% by weight, a pigment/binder ratio of 1:3, a pH of 3, organically bonded diphosphorous pentoxide in an amount of 4% by weight, based on the solids, and inorganically bonded disphosphorous pentoxide in an amount of 17% by weight, based on the solids. The
25 coating material 2 was fully stable on storage in the absence of actinic radiation for at least one month. It was outstandingly suitable for the production of primer coatings.

Examples 3 to 8

The production of primer coatings using the coating material 1 as per Example 1

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The substrates used were unpretreated HDG (hot dipped galvanized) steel panels from Chemetall.

10 In the case of Example 3, coating material 1 was applied in a film thickness of 4 to 6 μm . The water contained therein was evaporated at 80°C over one minute. The resulting film was cured with UV radiation in a dose of 1000 mJ cm^{-2} .

15 In the case of Example 4, coating material 1 was applied in a film thickness of 1 to 2 μm . The water contained therein was evaporated at 80°C over one minute. The resulting film was partially cured with UV radiation in a dose of 300 mJ cm^{-2} . The part-cured film
20 was coated with coating material 1 in a film thickness of 4 to 6 μm . The water contained therein was likewise evaporated at 80°C over one minute. The two films were then fully cured with UV radiation in a dose of 1000 mJ cm^{-2} .

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In the case of Example 5, coating material 1 was applied in a film thickness of 1 to 2 μm . The water contained therein was evaporated at 80°C over one minute. The resulting film was partially cured with UV

radiation in a dose of 300 mJ cm^{-2} . The part-cured film was coated with a commercial, solvent-free, UV-curable clearcoat material of series CD 97 from BASF Coatings AG in a film thickness of 4 to 5 μm . The two films were
5 then fully cured with UV radiation in a dose of 1000 mJ cm^{-2} .

All of the coatings of Examples 3 to 5 exhibited an outstanding overall appearance.

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For Examples 6 to 8, the coatings of Examples 3 to 5 were coated with a commercial solventborne coil coating topcoat material of series CD 27 from BASF Coatings AG. The topcoat films were cured thermally.

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The coated sample panels of Examples 3 to 8 were scribed and subjected to the salt spray test. After 168 hours the sample panels of Examples 3 to 5 still showed no adverse changes whatsoever, such as white
20 rusting or delamination. After 504 hours, the sample panels of Examples 6 to 8 also still showed no adverse changes, such as white rusting or delamination. This underscored the fact that the primary coatings had an outstanding corrosion protection effect.

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All of the coatings of Examples 3 to 7 could be deformed without problems and without damage (T-bend test: T1-1.5). The deformability of the coating of Example 8 was even better (T-bend test: T0-0.5).

The coatings of Examples 3 to 7 met the requirements of class IV of the specification of the company Usinor for components for outdoor use; the coating of Example 8
5 even met the requirements of the class VI specification.

Examples 9 to 14

- 10 **The production of primer coatings using the coating material 2 as per Example 2**

For Examples 9 to 14, Examples 3 to 8 were repeated but using the coating material 2 as per Example 2 instead
15 of the coating material 1 as per Example 1. The results obtained were the same outstanding results as in the case of Examples 3 to 8.